Determination of Markers of Particulate Matter in Environmental Tobacco Smoke

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Background/Purpose. To establish a suitable analytical method for measuring surrogate markers of particulate matter in environmental tobacco smoke (ETS) in different public areas.

Methods. The analytical procedures used in this study were based on those described by Ogden (1996). In brief, the optimum absorbance wavelengths of three particulate markers (UVPM, FPM and SolPM) were determined using an HPLC-photodiol detector. Air samples were taken from several public areas (pubs, offices, Internet cafes, and nightclubs) using PTFE filters joined to XAD-4 adsorbent. The concentrations of each particulate marker and the concentration of nicotine in the air samples were then measured.

Results. The results showed that there was good recovery and reproducibility in determination of each of the three particulate markers in ETS. The detection limits for the three markers were 6.9 ng for UVPM, 53.3 ng for FPM and 11.6 ng for SolPM. The highest levels of nicotine (26.7 $\mu g/m^3$) and UVPM (12.46 $\mu g/m^3$) were in pubs, and the lowest levels of nicotine and UVPM were in non-smoking offices (1.99 $\mu g/m^3$ and 0.10 $\mu g/m^3$, respectively). There was a high fluctuation in the levels of the three particulates and in the level of nicotine within and between the different public areas. SolPM was only detected in pubs (9.64 $\mu g/m^3$) but was not detected in other public areas.

Conclusion. There was good linear correlation and reproducibility in determination for the three particulate markers in ETS. The analytical method used in this study was simple, quick and effective for simultaneously measuring UVPM, FPM and SolPM in ETS. **(Mid Taiwan J Med 2008;13:122-9)**

Key words

analytical method, ETS, public areas, surrogated particulates

INTRODUCTION

Environmental tobacco smoke (ETS) is an important component of indoor air pollution. When cigarettes are being smoked, particulate mass levels rise substantially [1]. ETS is now considered an unacceptable and entirely preventable public health hazard, and public policy increasingly discourages the presence of tobacco smoke in the public domain [2,3]. Several studies have reported on airborne ETS generated by cigarettes from different indoor environments in the United States, Canada, and the United Kingdom [4-6]. The three most widely used markers of ETS-respirable particulate matter for apportionment are ultraviolet particulate matter (UVPM), fluorescent particulate matter (FPM) and solanesol particulate matter (SolPM). Analysis of ETS particles begins by collecting samples of ETS with a filter cassette containing a PTFE membrane filter. UVPM is analyzed by

Received : 3 January 2008. Revised : 30 March 2008.
Accepted : 9 April 2008.

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extracting it from the PTFE membrane filter with methanol followed by measuring its absorbance at 325 nm. FPM is measured using fluorescence detection ($\lambda_{excitation}$ = 300 nm, $\lambda_{emission}$ = 420 nm). SolPM is measured by liquid chromatography (LC) UV detection (λ = 205 nm) in an aliquot of the methanol extract [7-9]. Studies that have assessed ETS and markers of particulates in indoor air in several European cities found the following trend in markers of ETS-respirable particulate matter: UVPM > FPM > SolPM [10,11]. There were consistent ratios of the levels of these markers to the levels of respirable suspended particulates (RSP). Estimates of ETS particulates in indoor air showed a good correlation with airborne SolPM and FPM, and moderate correlation with airborne UVPM and SolPM/FPM estimates.

The prevalence of smoking in Taiwan has continued to increase over the past ten years. The prevalence of smoking among men and women in Taiwan is around 50% and 6%, respectively, although the number of female smokers is increasing at the fastest rate [12]. Lung cancer is the leading cause of death among female cancer patients in Taiwan. In 1997, the Tobacco Control Act was introduced in Taiwan in order to reduce indoor ETS levels. Only one study has assessed indoor particulate levels in ETS in Taiwan. Cheng [13] found that SolPM levels in pool halls in Taipei city ranged from 0.26 $\mu g/m^3$ to 9.91 $\mu g/m^3$ (mean = 3.03 $\mu g/m^3$); however, they did not simultaneously determine the levels of other particulates in ETS. It is necessary to establish an appropriate analytical method for measuring the levels of surrogate particulate matter and vapor in ETS. The purpose of the current study was to set up the optimal analytical conditions for simultaneously determining levels of three particulate markers in ETS as well as to measure the levels of particulates in different public buildings.

MATERIALS AND METHODS

Selection of public buildings

We took air samples using a PTFE filter and an XAD-4 sorbent cartridge from the following buildings: two pubs, three smoking offices, two non-smoking offices, one Internet café, and one nightclub. The managers of the buildings gave oral consent to the study. Temperature, the type of ventilation system, the humidity level, number of smokers and area size were recorded at the time of the sampling.

Analytical method of three particulates markers and airborne nicotine from ETS

The analytical procedures used in this study to measure three particulate markers (UVPM, FPM and Solanesol) in ETS were based on those described by Ogden [7,8]. 2,2',4-4 tetrahydroxyl-benzophenone was used to represent UVPM levels. Scopoletin and solanesol were used to represent levels of FPM and SolPM, respectively. The optimum absorbance wavelengths of the three particulate markers were determined using spectrophotometry. The results were as follows: UVPM =321 nm, FPM = 206 nm; SolPM = 209.5 nm. In order to determine the ideal buffer solution, three salts were tested (NaCl, KH_2PO_4, NaOH). NaOH showed the best resolution. The pretreatment method for collection of the three particulates from the PTFE filter was as follows. Two milliliters of methanol was poured through the PTFE filter to extract an aliquot of three particulates, which was then vibrated for 10 min. A PVDF membrane (pore size = 0.45 μm) was then used to filter the aliquot. A 1 mL aliquot was analyzed using an HPLC-photodial detector (HP 1100- G1315A, Detector : DAD 210 nm & 300 nm). The column used for separation was the Supelco LC-8 ID (4.6 mm × 250 mm). The mobile phase comprised methanol and glacial acetic acid (ratio = 99.9% : 0.1%). NaOH was added to adjust the pH value to 6.5. The flow rate was 0.6 mL/min and the injection volume was 100 μL. Each analysis took about 12 min to complete. To assess levels of nicotine, the adsorbent XAD-4 was used to collect the nicotine, which was then extracted from the sample with 1mL of acetic ester. For the internal standard, 100 μL of quinonine was added and mixed thoroughly. GC-NPD was used to determine nicotine levels. The column used was DB-WAX (30 m × 0.25 mmID). The oven

temperature was set at 110°C (for 2 min); it was then increased by 20°C per minute until it reached 150°C (for 6 min). It was then increased by 30°C per minute until the temperature reached 240°C (for 1 min).

Two calibration curves (high and low) were established for each of the three particulates. The UVPM levels ranged from 13.65 to 548.6 µg/mL and from 0.55 to 27.16 µg/mL, respectively. The FPM levels ranged from 10.01 to 408.6 µg/mL and from 0.55 to 20.43 µg/mL, respectively. The SolPM levels ranged from 5.82 to 234.3 µg/mL and from 0.23 to 11.59 µg/mL, respectively. Nicotine levels ranged from 77.05 to 1669.1 µg/mL and from 3.64 to 151.74 µg/mL. For each of the calibration curves, correlation coefficients exceeded 0.995. Limits of detection (LOD) using HPLC and GC (gas chromatography) were as follows: UVPM = 6.9 ng; FPM = 53.3 ng; SolPM = 11.6 ng and nicotine = 5.42 ng. LOD was determined as the mean +3 SDs of the samples.

Quality control of analytical method

Stability of each of the three surrogate particulates in the PTFE filter was tested at 4°C and at room temperature (24°C). Concentrations of stock solutions of the three particulate markers were as follows: UVPM = 10.49 µg/mL; FPM = 10.75 µg/mL; SolPM = 3.64 µg/mL. A volume of 100 µL of each solution was homogeneously spiked into the filter and stability was tested in triplicate on days 1, 3, 5, 7, 14, and 21. For FPM, 92.9% was recovered at room temperature on day 14. Recovery of the other two compounds exceeded 95% at room temperature on day 14. Stability at 4°C was higher than at room temperature for all compounds. All analyses were completed within seven days after collection of the samples. The compounds were stable for up to 21 days at 4°C and at 24°C.

RESULTS

Table 1 shows the reproducibility within and between days for the three particulate markers in ETS. The coefficient of variation (CV) in the peak area was higher than the retention time (RT). CV values were higher between days than within days. None of the CV values for the three surrogate markers or nicotine exceeded 5%. Table 2 shows the recovery efficiencies of the three particulate markers in ETS. High and low levels were tested and all recovery efficiencies exceeded 93%. Recovery efficiency was highest for SolPM and lowest for UVPM. HPLC retention times (RT) were 4.79 min for UVPM and 5.38 min for FPM. RT for SolPM was 9.21 min. It was difficult to completely separate the UVPM and FPM obtained from the air samples,

Table 1. Reproducibility (%) within and between days for the three surrogated particulates in environmental tobacco smoke

	UVPM		FPM		SolPM	
Level (µg/mL)	27.15		20.43		11.70	
	RT	Area	RT	Area	RT	Area
Within days	4.75 ± 0.01*	899.70 ± 7.27	5.35 ± 0.01	517.10 ± 1.74	9.18 ± 0.02	1396.2 ± 5.99
CV (%)	0.18	0.81	0.27	0.34	0.18	0.43
Between days	4.78 ± 0.013	911.13 ± 29.12	5.30 ± 0.05	514.92 ± 8.67	9.22 ± 0.06	1368.21 ± 14.04
CV (%)	0.27	3.20	0.99	1.68	0.66	1.03

*Mean ± SD. UVPM = ultraviolet particulate matter; FPM = fluorescent particulate matter; SolPM = solanesol particulate matter; RT = retention time (minute); CV = coefficient of variation.

Table 2. Recovery efficiencies (%) at low and high concentrations (µg/mL) for the three surrogated particulates in ETS (N = 3)

	UVPM		FPM		SolPM	
Level (µg/mL)	12.46	0.34	9.28	0.20	5.32	0.29
Recovery efficiencies (%)	93.5 ± 5.5*	93.1 ± 1.0	98.9 ± 0.9	95.3 ± 2.4	97.6 ± 0.7	98.7 ± 2.7

*Means ± SD. UVPM = ultraviolet particulate matter; FPM = fluorescent particulate matter; SolPM = solanesol particulate matter.

although they were clearly identifiable on the chromatograms.

Samples of airborne particulate markers and nicotine in ETS from various types of buildings were taken and analyzed (Table 3). There was wide variation in levels of ETS compounds within the individual buildings and among the buildings. The highest levels of the three particulate markers and nicotine were in the two nightclubs. UVPM levels were highest, followed by SolPM and FPM. The mean nicotine level in the two nightclubs was 26.7 μg/m^3 (range = 7.12-36.76 μg/m^3). Both of the nightclubs had poor ventilation systems and a large number of smokers with no separate areas for non-smokers. Even in the buildings that provided non-smoking areas, such as restaurants and offices, the ventilation systems appeared to distribute the ETS evenly throughout the building. Levels of UVPM, FPM and nicotine were significantly higher in the smoking offices than in the non-smoking offices. SolPM was not detected in either type of office.

DISCUSSION

In this study, we used a convenient and simple method for measuring the levels of particulate markers in environmental tobacco smoke. Methanol was used to extract the compounds from the filters, and then the compounds were filtered and analyzed. After four hours of air sampling, LOD for UVPM, FPM and SolPM were 0.014, 0.111 and 0.024 μg/m^3, respectively. The lowest LOD values for UVPM, FPM and SolPM after eight hours of sampling were 0.49, 0.25 and 0.0012 μg/m^3, respectively [14]. The LOD values for UVPM, FPM and SolPM were 1.5, 0.2 and 2.0 μg/m^3, respectively [15]. The limits of quantitation (LOQ) at 8.5 hours for UVPM, FPM and SolPM were 1.33, 0.31 and 0.71 μg/m^3, respectively. However, the wide range of results reported may be attributed to the different analytical methods employed and the definitions of the LOD used [16]. The airborne nicotine detection limit in the present

Table 3. Levels (μg/m^3) of the three surrogate particulates and nicotine in ETS in each of the public buildings

Public building	n	Mean ± SD	Range
Pub			
UVPM	12	12.45 ± 18.25	0.38-45.75
FPM		2.12 ± 3.10	0.07-7.77
SolPM		9.64 ± 1.52	8.46-13.16
Nicotine		26.74 ± 7.92	7.12-36.76
Smoking office			
UVPM	9	7.78 ± 11.63	0.03-26.65
FPM		1.32 ± 1.98	0.01-4.49
SolPM		ND	
Nicotine		14.85 ± 38.04	0.85-116.23
Non-smoking office			
UVPM	4	0.10 ± 0.03	0.06-0.13
FPM		0.02 ± 0.01	0.01-0.02
SolPM		ND	
Nicotine		1.99 ± 0.96	1.07-3.11
Internet cafe			
UVPM	2	0.39 ± 0.04	0.37-0.43
FPM		0.07 ± 0.01	0.06-0.07
SolPM		ND	
Nicotine		14.35 ± 2.87	12.32-16.38
Nightclub			
UVPM	6	0.39 ± 0.16	0.27-0.69
FPM		0.07 ± 0.03	0.05-0.12
SolPM		ND	
Nicotine		6.47 ± 1.57	3.74-8.07

UVPM = ultraviolet particulate matter; FPM = fluorescent particulate matter; SolPM = solanesol particulate matter; ND = nondetectable.

study (0.011 μg/m^3) is lower than the limits reported by Ogden (0.026 μg/m^3) [16] and Phillips (0.27 μg/m^3) [15].

Neither nicotine nor UVPM had a strong correlation with RSP. Nicotine levels correlated with other gas-phase constituents in ETS. UVPM and other surrogate constituents were suitable markers of particle-phase ETS [9]. Numerous studies [10,11,15] have tried to measure respirable suspended particles (RSP) in ETS. ETS comprises combustion-derived particulates, including single- and multi-ring aromatic compounds, which absorb UV light. Some of these compounds may be overestimated as they may not all be derived solely from ETS. For example, combustion-derived aerosols may be present in the environment, such as those from wood-burning stoves, kerosene heaters and diesel exhaust. Using HPLC with a UV detector, we determined the levels of 2,2', 4-4' tetrahydroxy-benzophenone in this study. Ogden and Maiolo [16] simultaneously determined UVPM and FPM using a fluorescent detector in series with a UV detector on the HPLC system; they did not, however, measure SolPM values. However, SolPM is distributed throughout almost 100% of the particle phase of tobacco smoke and is not known to be produced by sources other than tobacco combustion. It is necessary to develop a timesaving and convenient method to simultaneously measure levels of UVPM, FPM and SolPM in ETS.

Generally speaking, there is only one ventilation system used in most buildings in Taiwan, regardless of whether the buildings contain offices which allow smoking or offices which do not allow smoking. In this study, we found that nicotine levels in the non-smoking areas were higher than those reported in previous studies. For example, the mean nicotine level on a weekday in a non-smoking office was 0.25 μg/m^3 in the USA [17]. Mean indoor nicotine levels in offices were 2.5 and 4.8 μg/m^3 in restaurants in South Korea [14]. Moschandreas [18] reviewed studies on pollutant concentrations in various hospitality environments and found that nicotine levels were consistently higher in smoking areas than in non-smoking areas, although there was high fluctuation of results. Mean nicotine levels in jazz clubs in Sweden (37.0 μg/m^3) [19] were higher than those found in the nightclubs in the present study (6.47 μg/m^3). Nicotine and SolPM levels (106 and 18 μg/m^3) in discotheques reported by Tang [20] were higher than in the nightclubs in this study (26.7 and 9.6 μg/m^3). In the only other study in Taiwan to measure levels of SolPM, Cheng [13] reported that levels of SolPM in ETS in pool halls was 3.03 μg/m^3.

Chan [21] reported that the indoor nicotine levels in homes was 0.7 μg/m^3 in both winter and summer. Yang and Kuo [22] reported that the mean nicotine level in a pub was 597 μg/m^3, exceeding the limit set by the ACGIH TWA occupational standards (500 μg/m^3). The number of households with no or partial smoking bans correlated significantly with urine cotinine levels (r = 0.49) [3]. In Taiwan, there is an urgent need for an indoor air quality standard similar to the ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) 62-1989 Ventilation Standard, particularly for pubs and discotheques in Taiwan, which typically have high levels of ETS and poor ventilation. The Taiwan DOH enacted a smoking ban in public buildings in 1997, with a penalty of NT$ 500 for non-compliance. However, there has been lax enforcement of this law and the small fine has proved to be an ineffective deterrent. In addition, there is often no provision for smoking rooms in public areas. In the current study, particulate markers in ETS were detected in significant amounts even in areas designated as non-smoking areas. If the Taiwan government wants to reduce the levels of particulate markers and nicotine from ETS, it should call for concerted efforts to increase awareness of this public health problem and enforce regulations aimed at protecting non-smokers.

In conclusion, our method for simultaneously measuring UVPM, FPM and SolPM levels in ETS is quick, convenient and accurate. The field study showed that in pubs

in Taiwan, the particulate markers with the highest levels were UVPM SolPM, and FPM, respectively. Non-smoking offices had the lowest levels of all three markers and nicotine. More studies are needed to measure ETS in public buildings, especially in non-smoking indoor environments that use the same ventilation system as smoking environments.

ACKNOWLEDGMENTS

Special thanks are owed to the China Medical University (CMC91-EM-01) for funding this research and for assistance in conducting this study.

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分析空氣中二手菸粒狀物指標之濃度

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背景/目的　本研就之目的在建立二手菸中粒狀物指標之方法，並測定在公共場所內二手菸之濃度。

方法　分析步驟係參考Ogden (1996)之方法，針對二手菸中三種粒狀物之指標物質以高效率液相層析儀(HPLC-photodial)進行分析。再選擇台中市常見之公共場所(包括pubs、辦公大樓、網咖及舞廳)，以PTFE濾紙採集三種代理粒狀物及XAD-4採集管氣態尼古丁進行環境採樣。

結果　分析三種粒狀污染物之指標均有良好回收率及再現性，其中分析UVPM、FPH及SolPM之偵測極限爲6.9、53.3及11.6 ng。在公共場所中以pubs之尼古丁(26.7 μg/m^3)及UVPM濃度(12.46 μg/m^3) 最高，非吸菸辦公大樓最低，分別爲1.99及0.10 μg/m^3。然而，三種粒狀物質指標及氣狀尼古丁濃度在各公共場所之濃度有很大的變異性，其中只有pubs可偵測到SolPM (9.64 μg/m^3)，但在其他公共場所卻無法測到此物質。

結論　本研究方法可得到良好線性及再現性，亦可作爲簡單、快速及同時分析三種二手菸粒狀物之指標(UVPM、FPM及SolPM)方法，可當作國內測定公共場所暴露二手菸粒狀物質濃度方法之參考。（**中台灣醫誌2008;13:122-9**）

關鍵詞

測定方法，粒狀物指標(UVPM, FPM, SolPM)，公共場所，二手菸

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收文日期：2008年1月3日　　修改日期：2008年3月30日

接受日期：2008年4月9日